

FORM PTO-1300 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

UDX

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/088655

INTERNATIONAL APPLICATION NO.

PCT/IL99/00510

INTERNATIONAL FILING DATE

September 22, 1999

PRIORITY DATE CLAIMED

TITLE OF INVENTION

SUBSTRATE COATING FOR IMPROVED TONER TRANSFER AND ADHESION

APPLICANT(S) FOR DO/EO/US

Yaacov ALMOG et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/ISA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Amendments to the claims of the International Application under PCT Article 34 are transmitted herewith as annexes to the IPR.

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/088655)		INTERNATIONAL APPLICATION NO. PCT/IL99/00510		ATTORNEY'S DOCKET NUMBER UDX	
24. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO				\$1040.00	
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO				\$890.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO				\$740.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)				\$710.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)				\$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =					
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				\$890.00	
				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	56 - 20 =	36	x \$18.00	\$648.00	
Independent claims	2 - 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$1,538.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$1,538.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				\$0.00	
TOTAL NATIONAL FEE =				\$1,538.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$1,538.00	
				Amount to be: refunded	\$
				charged	\$
<p>a. <input type="checkbox"/> A check in the amount of _____ to cover the above fees is enclosed.</p> <p>b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 03-3419 in the amount of \$1,538.00 to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 03-3419. A duplicate copy of this sheet is enclosed.</p> <p>d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.</p>					
<p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p>SEND ALL CORRESPONDENCE TO:</p> <div style="border: 1px solid black; padding: 5px; width: 45%;"> <p>William H. Dippert, Esq. Cowan, Liebowitz and Latman, P.C. 1133 Avenue of the Americas New York, NY 10036-6799</p> <p>Tel: (212) 790-9200</p> </div> <div style="width: 55%;"> <p style="text-align: right;"><i>Paul Fenster</i></p> <p>SIGNATURE</p> <hr/> <p>Paul FENSTER</p> <p>NAME</p> <hr/> <p>33,877</p> <p>REGISTRATION NUMBER</p> <hr/> <p>March 13, 2002</p> <p>DATE</p> <hr/> </div>					

UDX A01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Y. ALMOG, et al.
Serial Number: Not Yet Assigned
Filed: 22 September 1999 as PCT/IL99/00510 and Herewith as US National Stage
For: Substrate Coating for Improved Toner Transfer and Adhesion
Art Unit: Not Yet Assigned
Examiner: Not Yet Assigned

Honorable Commissioner of Patents and Trademarks
Washington DC 20231

PRELIMINARY AMENDMENT

Sir:

Further to the concurrent filing of the U.S. national stage of PCT/IL99/00510, kindly amend the application as follows prior to examination:

IN THE SPECIFICATION

Kindly add the following section, on page 1, immediately after the title:

--RELATED APPLICATIONS

The present application is a US national application of PCT Application No. PCT/IL99/00510, filed on September 22, 1999.--

IN THE CLAIMS

Kindly cancel claims 25, 27, 58 and 59, without prejudice. Kindly amend claims 4, 5, 10, 14-16, 21, 23, 24, 26, 28-31, 36, 37, 42, 46-48, 53, 55-57 and 60 in accordance with the following clean claims.

4. (Amended) A printing method according to claim 1 wherein the coating is UV cured.
5. (Amended) A printing method according to claim 1 wherein the coating comprises at least 30% silica.
10. (Amended) A printing method according to claim 1 wherein the silica has a size of between 5 and 50 nanometers.

UDX A01

14. (Amended) A printing method according to claim 1 wherein the silica is not chemically bonded to the rest of the coating.
15. (Amended) A printing method according to claim 1 wherein the silica is chemically bonded to the rest of the coating.
16. (Amended) A printing method according to claim 1 wherein the coating further comprises an anchorage agent.
21. (Amended) A printing method according to claim 18 wherein the substance is Poly(propylene oxide).
23. (Amended) A printing method according to claim 1 wherein the substrate and the pigmented particles are both acidic.
24. (Amended) A printing method according to claim 1 wherein the substrate is coated with a polyamide coating between the coating containing silica and the substrate.
26. (Amended) A printing method according to claim 1 wherein the material of the substrate is chosen from the group consisting of PET, PVC and polycarbonate.
28. (Amended) A printing method according to claim 1 wherein the coating forms a substantially smooth surface.
29. (Amended) A printing method according to claim 1 wherein the substrate is a sheet of material.
30. (Amended) A printing method according to claim 1 wherein the substrate is a disk.
31. (Amended) A printing method according to claim 1 wherein the surface of the coating is film.
36. (Amended) A coated substrate according to claim 33 wherein the coating is UV cured.

UDX A01

37. (Amended) A coated substrate according to claim 33 wherein the coating comprises at least 30% silica.

42. (Amended) A coated substrate according to claim 33 wherein the silica has a size of between 5 and 50 nanometers.

46. (Amended) A coated substrate according to claim 33 wherein the silica is not chemically bound to the rest of the coating.

47. (Amended) A coated substrate according to claim 33 wherein the silica is chemically bound to the rest of the coating.

48. (Amended) A coated substrate according to claim 33 wherein the coating further comprises an anchorage agent.

53. (Amended) A coated substrate according to claim 50 wherein the substance is Poly(propylene oxide).

55. (Amended) A coated substrate according to claim 33 wherein the substrate is acidic.

56. (Amended) A coated substrate according to claim 33 wherein the substrate is coated with a polyamide coating between the coating containing silica and the sheet.

57. (Amended) A coated substrate according to claim 33 wherein the material of the sheet is chosen from the group consisting of PVC, PET and polycarbonate.

60. (Amended) A coated substrate according to claim 33 wherein the coating is smooth.

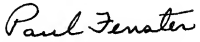
REMARKS

The present application is a US national application of PCT Application No. PCT/IL99/00510. The present amendments, based on the claims attached to the IPER, have been made to place the application in proper US form. The application contains claims 1-24, 26, 28-57 and 60. Claims 25, 27, 58 and 59 have been canceled.

UDX A01

A marked up copy of the amended claims is attached hereto.
An action on the merits is respectfully awaited.

Respectfully submitted,
Y. Almog, et al.



Paul FENSTER
Reg. No. 33,877

March 13, 2002
William H. Dippert, Esq.
Cowan, Liebowitz and Latman, P.C.
1133 Avenue of the Americas
New York, NY 10036-6799

Tel: (212) 790-9200

UDX A01

MARKED UP AMENDED CLAIMS

4. (Amended) A printing method according [any of the preceding claims] to claim 1 wherein the coating is UV cured.
5. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the coating comprises at least 30% silica.
10. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the silica has a size of between 5 and 50 nanometers.
14. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the silica is not chemically bonded to the rest of the coating.
15. (Amended) A printing method according to [any of claims 1-13] claim 1 wherein the silica is chemically bonded to the rest of the coating.
16. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the coating further comprises an anchorage agent.
21. (Amended) A printing method according to [any of claims 18-20] claim 18 wherein the substance is Poly(propylene oxide).
23. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the substrate and the pigmented particles are both acidic.
24. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the substrate is coated with a polyamide coating between the coating containing silica and the substrate.
26. (Amended) A printing method according to [any of claims 1-24] claim 1 wherein the material of the substrate is chosen from the group consisting of PET, PVC and polycarbonate.

UDX A01

28. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the coating forms a substantially smooth surface.

29. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the substrate is a sheet of material.

30. (Amended) A printing method according to [any of claims 1-28] claim 1 wherein the substrate is a disk.

31. (Amended) A printing method according to [any of the preceding claims] claim 1 wherein the surface of the coating is film.

36. (Amended) A coated substrate according [any of claims 33-35] to claim 33 wherein the coating is UV cured.

37. (Amended) A coated substrate according to [any of claims 33-36] claim 33 wherein the coating comprises at least 30% silica.

42. (Amended) A coated substrate according to [any of claims 33-41] claim 33 wherein the silica has a size of between 5 and 50 nanometers.

46. (Amended) A coated substrate according to [any of claims 33-45] claim 33 wherein the silica is not chemically bound to the rest of the coating.

47. (Amended) A coated substrate according to [any of claims 33-45] claim 33 wherein the silica is chemically bound to the rest of the coating.

48. (Amended) A coated substrate according to [any of claims 33-46] claim 33 wherein the coating further comprises an anchorage agent.

53. (Amended) A coated substrate according to [any of claims 50-52] claim 50 wherein the substance is Poly(propylene oxide).

UDX A01

55. (Amended) A coated substrate according to [any of claims 33-54] claim 33 wherein the substrate is acidic.

56. (Amended) A coated substrate according to [any of claims 33-54] claim 33 wherein the substrate is coated with a polyamide coating between the coating containing silica and the sheet.

57. (Amended) A coated substrate according to [any of claims 33-56] claim 33 wherein the material of the sheet is chosen from the group consisting of PVC, PET and polycarbonate.

60. (Amended) A coated substrate according to [any of claims 33-59] claim 33 wherein the coating is smooth.

WO 01/22172

SUBSTRATE COATING FOR IMPROVED TONER TRANSFER AND ADHESION

FIELD OF THE INVENTION

This invention is concerned with primers used for printing and more particularly with primers that have high affinity for both the ink and plastic such as used in substrates and compact disks (CD's).

BACKGROUND OF THE INVENTION

Primers or binders are generally necessary when printing with liquid toners on some plastic materials, such as PET, polycarbonate or other substrates. Without binders, such toners do not adhere well to the surface to be printed upon. Thus, a binder material is needed that has a high affinity for both the toner and the plastic. In the past, solvent based primers were used. However, the solvents in use are not environmentally friendly and are therefore commercially problematic.

However, it is difficult to provide a primer that is environmentally friendly and nonetheless has a high affinity for both the toner and the plastic. In general, it has been found that binders which are applied dissolved in solvents, which evaporate and leave a cured binder work best for this task. Such binders are generally acrylates. However, such primer systems do cause air pollution when the solvents evaporate.

Primers which are UV cured and/or applied in an aqueous solution are advantageous since they are non-polluting. Acrylic based monomers are known for use as UV cured binders. It is known to use hyrolized PVA (applied as a aqueous solution) for a binder. However, such binders, while they adhere well to plastic substrates, do not adhere well to toners such as those based on Nucrel (copolymers of ethylene and an alpha, beta ethelenically susaturated acid of either acrylic or metaacrylic acid by E. I. du Pont) and Surlyn (ionomer resins by E. I. du Pont) polymers. Such polymer based toners are sold, for example, by Indigo, N.V. of the Netherlands under the trade name ElectroInk. The ElectroInk brand toners comprise pigmented polymer particles, a carrier liquid such as a Isopar (solvent of branched-chain aliphatic hydrocarbons and mixtures thereof, e.g., isoparaffinic hydrocarbon fractions by EXXON) or Marcol (highly refined petroleum oils by EXXON).

SUMMARY OF THE INVENTION

An aspect of the invention is concerned with the modification of presently available binders which are not solvent based to improve the adhesion of toner materials to them.

In some preferred embodiments of the invention, these available binders are acrylic based monomers. In some preferred embodiments of the invention, the available binders are UV cured. In some preferred embodiments of the invention, the binders are not dissolved in

WO 01/22172

PCT/IL99/00510

organic solvents when they are applied. In some preferred embodiments of the invention, the binders have more than one of these characteristics.

An aspect of some preferred embodiments of the invention is concerned with the provision of a UV cured binder which has high adhesion to plastic substrates and also to toner materials, such as the aforementioned ElectroInk brand materials.

In a preferred embodiment of the invention, the binder comprises a high concentration of a material which absorbs the carrier liquid. In preferred embodiments of the invention, nano-silica (5-50 nanometers) is used as the absorber. Such particles should be preferably present in a concentration of at least 25 percent, more preferably between 30 and 50 percent and most preferably 35 and 45 percent. These percentages are by weight of total solids after curing.

While the exact operation of this absorber material is not known, it is believed that the addition of this material to the binder and the subsequent drawing of the toner to the binder by the material enables close approach of the toner polymer to the binder, such that strong, but very short range, Van der Waals forces take effect. Such forces strongly bind the toner polymer to the binder. Without the addition of the material, repulsion caused by the acid nature of both toner particles and binder is believed to mitigate the effect of such forces. However, the exact nature of the mechanism that obviates the use of said binders in the prior art is not yet established.

In a preferred embodiment of the invention, anchorage agents such as an amine material, especially diamine terminated polyoxyethelene, diamene, triamine or monoamine terminated Polypropylene oxide, are added to the binder coatings to increase their adhesion to the toner materials. Other anchorage agents can also be used, especially those with an amino terminated polymer backbone.

In a preferred embodiment of the invention, the binders comprise acrylic based UV curable monomers with mono, di and tri functionality. As indicated above, such binders, by themselves, are generally ineffective for use with negatively charged toners.

An aspect of some preferred embodiment of the invention is concerned with the addition of carrier liquid absorbing materials such as nano-silica, to other, non-UV cured binder materials such as, for example, water soluble hydrolized PVA. It was found that at high proportions of nano-silica, such as for example 25 percent or more by weight of total solids, the coating started to become "tonerphilic", in terms of transfer and adhesion to the binder.

There is thus provided, in accordance with a preferred embodiment of the invention, a printing method comprising:

WO 01/22172

PCT/IL99/00510

providing a substrate having a surface coated with a coating comprising at least 25% silica; and

printing on the coated surface with an ink comprising pigmented polymer particles and a carrier liquid.

5 Preferably the coating comprises an acrylic material, for example a cross-linked polyacrylic ester.

Preferably, the coating is UV cured.

In various preferred embodiments of the invention the silica content of the coating comprises at least 30% silica, at least 35% silica, at least 40% silica, at least 45% silica and at
10 least 50% silica.

In various preferred embodiments of the invention the silica has a size of between 5 and 50 nanometers, between 10 and 40 nanometers, between 10 and 20 nanometers or about 16 nanometers.

In a preferred embodiment of the invention, the silica is not chemically bonded to the
15 rest of the coating. Alternatively, the silica is chemically bonded to the rest of the coating.

Preferably the coating further comprises an anchorage agent. Preferably, the anchorage agent comprises an amine material. Preferred amine materials include diamine, monoamine and triamine terminated substances. Preferably the substance is Poly(propylene oxide) or Poly-oxylthelene.

20 In a preferred embodiment of the invention, the substrate and the pigmented particles are both acidic.

In a preferred embodiment of the invention the substrate is coated with a polyamide coating between the coating containing silica and the substrate.

In various preferred embodiments of the invention, the substrate is PVC, PET or
25 Polycarbonate.

Preferably, the coating forms a substantially smooth surface.

In a preferred embodiment of the invention, the substrate is a sheet of material. In an alternative preferred embodiment it is a disk, such as a CD disk.

There is further provided a substrate comprising:

30 a sheet of polymer; and

a substantially smooth printable coating on the polymer sheet comprising at least 25% silica.

Preferably the coating comprises an acrylic material, for example a cross-linked polyacrylic ester.

WO 01/22172

PCT/IL99/00510

Preferably, the coating is UV cured.

In various preferred embodiments of the invention the silica content of the coating comprises at least 30% silica, at least 35% silica, at least 40% silica, at least 45% silica and at least 50% silica.

5 In various preferred embodiments of the invention the silica has a size of between 5 and 50 nanometers, between 10 and 40 nanometers, between 10 and 20 nanometers or about 16 nanometers.

In a preferred embodiment of the invention, the silica is not chemically bonded to the rest of the coating. Alternatively, the silica is chemically bonded to the rest of the coating.

10 Preferably the coating further comprises an anchorage agent. Preferably, the anchorage agent comprises an amine material. Preferred amine materials include diamine, monoamine and triamine terminated substances. Preferably the substance is Poly(propylene oxide) or Poly-oxyethelene.

In a preferred embodiment of the invention, the substrate is acidic.

15 In a preferred embodiment of the invention the substrate is coated with a polyamide coating between the coating containing silica and the substrate.

In various preferred embodiments of the invention, the substrate is PVC, PET or Polycarbonate.

Preferably, the coating forms a substantially smooth surface.

20 There is further provided, in accordance with a preferred embodiment of the invention, a composition of matter comprising an acrylic monomer material comprising between 40% and 75% of the composition; and silica, in an amount exceeding 25% of the composition, which silica is not chemically bound to the monomer.

Preferably, the acrylic material comprises an acrylic ester.

25 Preferably, the monomer is UV curable.

In various preferred embodiments of the invention the silica content of the composition comprises at least 30% silica, at least 35% silica, at least 40% silica, at least 45% silica and at least 50% silica.

30 In various preferred embodiments of the invention the silica has a size of between 5 and 50 nanometers, between 10 and 40 nanometers, between 10 and 20 nanometers or about 16 nanometers.

In a preferred embodiment of the invention, the silica is not chemically bonded to the rest of the composition. Alternatively, the silica is chemically bonded to the rest of the composition.

WO 01/22172

PCT/IL99/00510

Preferably the composition further comprises an anchorage agent. Preferably, the anchorage agent comprises an amine material. Preferred amine materials include diamine, monoamine and triamine terminated substances. Preferably the substance is Poly(propylene oxide) or Poly-oxylthelene.

The invention will be more clearly understood with reference to the following non-limiting examples of preferred embodiments thereof.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is believed to be applicable to a wide range of binder materials, substrates and toner materials. Some representative, non-limiting, examples of the application of the present invention follow.

Example 1

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in UV curable acrylic esters (Cray Valley Pro 2698). Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5 and 50 nanometers are also believed to be useful in the practice of the invention. Since the addition of silica to the acrylic monomer increases its viscosity, isopropyl alcohol (IPA) was added to the dispersion so that it could be coated onto a substrate. A wide range of acrylic esters are useful in the practice of the invention.

The dispersions were wire rod coated on 330 micrometer thick PVC sheets pre-coated with PA polyamide (Mazzuccelli) and exposed to light from a UV mercury lamp which provides 118 watts/cm and passes the light source at a velocity of about 8.64 cm/sec or about 13.6 joules/cm². (A lamp having a power of 300 w/inch and motion of the substrate at a rate of 17 ft/min.) The resulting coated material was used as a substrate, for ElectroInk™ type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of Indigo™, N.V., on an Omnius™ CardPress™ printer of the same company. In this printer a liquid toner image is developed on a photoreceptor and transferred to an intermediate transfer member for subsequent transfer to the substrate by heat and pressure. During the second transfer process the image is also fused and fixed to the substrate.

The tested formulations (all parts are by weight) and the results are:

WO 01/22172

PCT/IL99/00510

	Parts Acrylic Ester	Parts Silica	Parts IPA	NVS	Results
Control 1	10	0	1	91%	No transfer to substrate
Control 2	8	0	3	73%	No transfer to substrate
A	10.4	1 (9%)	1	92%	No transfer to substrate
B	5	1 (16.7%)	1.75	77.5%	Traces of ink transferred
C	2.5	1 (29%)	2	64%	Good transfer and fixing
D	1.5	1 (40%)	1.75	60%	Good transfer and fixing

In the table, NVS is the percentage of non-volatile solids in the coating mixture and the percentages under silica are percent silica of the NVS. All proportions in these and other examples are by weight. For dispersion D, the coating was somewhat uneven due to the large amount of silica in the coating. However, the transfer and fixing were good. The fixing was poor immediately after transfer but improved to good within a week after printing. From the table it appears that the coating changes from "tonerophobic" to "tonerophilic" at about 25% silica loading and that when transfer is good so is fixing.

Example 2

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in an aqueous acrylic copolymer solution (Glascol LS16, Allied Colloids-about 30% NVS). Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5 and 50 nanometers are also believed to be useful in the practice of the invention. The dispersions were homogenized in a high shear mixer for 1-3 minutes. The dispersions were diluted with water for high proportions of silica, their viscosity made them difficult to homogenize.

The dispersions were wire rod coated onto PET films and dried at elevated temperature (about 60°C to form a film. The resulting coated material was used as a substrate, for ElectroInk™ type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of Indigo™, N.V., on an Omnium™ CardPress™ printer of the same company.

The following table summarizes the results:

	Total weight	Wt. acrylic	Wt. Silica	NVS	Results
A	180.3	52.5	5.3 (9%)	32%	Only traces of transfer
B	176.7	42	8.7 (17%)	29%	Only traces of transfer
C	158.2	36.8	11.2 (23%)	32%	Only traces of transfer
D	145	29	14.5 (33%)	31%	Good Transfer, Poor Fixing
E	170	22	15 (40%)	22%	Good Transfer, Good Fixing

WO 01/22172

PCT/IL99/00510

Coatings D and E resulted in a hazy, rather than clear coating. This may be acceptable for some applications. However, the haziness may be removed by overcoating the film with clear varnish, for example a UV cured varnish. This coating process results in the filling in of the unevenness of the surface caused by the silica, which results in the haziness of the coating.

From the table it appears that the coating changes from tonerophobic to tonerophilic at about 25-30% silica loading and that when fixing is good for loading of 35-40% or greater.

Example 3

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in an aqueous styrene-acrylic emulsion (Zinpol 280, Worlee-about 48% NVS). Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5 and 50 nanometers are also believed to be useful in the practice of the invention. The dispersions were homogenized in a high shear mixer for 1-3 minutes. The dispersions were diluted with water when for high proportions of silica, when their viscosity made them difficult to homogenize.

The resulting coated material was used as a substrate, for ElectroInk™ type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of Indigo™, N.V., on an Omnius™ CardPress™ printer of the same company.

The following table summarizes the results:

	Total weight	Wt. acrylic	Wt. Silica	NVS	Results
A	186.5	43.2	6.5 (13%)	27%	Suffer from Foaming
B	153.7	35	8.7 (20%)	28%	Suffer from Foaming
C	164	27.1	9 (25%)	22%	Only traces of transfer
D	140.3	22.6	11.3 (33%)	24%	Good Transfer, Fair Fixing
E	158.4	18.9	13.4 (42%)	20%	Good Transfer, Good Fixing

A and B suffered from foaming causing an uneven coating. C produced a transparent film, but transfer to it was poor. Coatings D and E resulted in a hazy, rather than clear coating. This may be acceptable for some applications. However, the haziness may be removed by overcoating the film with clear varnish. This coating process results in the filling in of the unevenness of the surface caused by the silica, which results in the haziness of the coating. From the table it appears that the coating changes from tonerophobic to tonerophilic at about 30% silica loading and that fixing is good starting at about 40% loading.

WO 01/22172

PCT/IL99/00510

Example 4

Various amounts of nano-silica (Aerosil R972 by Degussa) was dispersed in an aqueous PVA solution formed by dissolving polyvinyl alcohol (Aldrich 88% hydrolyzed- average molecular weight 85k-146k) in deionized water to give a 10% solution. Aerosil R972 is a nanometric hydrophobic silica material having a particle size of approximately 16 nanometers. Other sizes, such as between 5 and 50 nanometers are also believed to be useful in the practice of the invention. The dispersions were homogenized in a high shear mixer for 1-3 minutes. Water was added to reduce the viscosity when it was too high for coating.

The resulting coated material was used as a substrate, for ElectroInk™ type 3.1 ink (liquid toner comprising pigmented toner particles and carrier liquid) of Indigo™, N.V., on an Omnium™ CardPress™ printer of the same company.

The following table summarizes the results:

	Total weight	Wt. PVA	Wt. Silica	NVS	Results
A	204.5	15	4.5 (23%)	10%	Poor transfer, Very Poor Fixing
B	139	10	5 (33%)	11%	Fair Transfer, Poor Fixing
C	140	10	6 (37.5%)	11%	Fair Transfer, Poor Fixing
D	307	10	7 (41%)	6%	Good Transfer, Poor Fixing
E	209	10	9 (47.3%)	9%	Good Transfer, Good Fixing

From the table it appears that the coating changes from tonerophobic to tonerophilic at about 30% silica loading and that fixing is good only for loadings above about 45%.

Example 5

Highlink OG materials (Clariant) are liquid suspensions of grafted colloidal silica in 1,6-hexanediol diacrylate. Among other organosols which are available are OG 100 in which the organic modifier is 2-Hydroxyethyl methacrylate, OG 101 in which the organic modifier is 2-Hydroxyethyl acetate, OG 103 in which the organic modifier is 1,6-Hexanediol diacrylate and OG 108 in which the modifier is Tripropylene glycol diacrylate. Each of these materials is available in various proportions of modifier and silica, ranging from 30 to 50 percent silica by weight. Since the silica is grafted, the viscosity is lower than for mixtures of ungrafted silica.

To 89 grams of Highlink OG 103-53 (51±1% by weight silica) was added 10 grams of Irgacure 651 organic photo-initiator (Ciba) and the materials were mixed until the initiator was totally dissolved in the carrier of the Highlink material. To this mixture 10 grams of Poly(propylene oxide), diamine terminated (molecular weight 230-Scientific Polymer Products) was added to form a coating material.

WO 01/22172

PCT/IL99/00510

This coating material was used to polycarbonate disks (CDI, Ltd.) and Melinex 529 PET films (ICI) by screen printing using a 180 mesh/cm fabric screen. The coating was cured immediately by applying to it light from a 118 watts/cm UV/lamp source and passing the coating by the light source at a velocity of about 5.08 cm/sec or about 23.2 joules/cm² (A lamp having a power of 300 w/inch and motion of the substrate at a rate of 10 ft/min.) The coating weight was about 5.3 gm/m².

These coated materials were printed on the OmniumTM CardPressTM printer using ElectroInk type 3.1 ink. Transfer and fixing were excellent. Variations of the amounts of additives (diamine 5-20% by weight of the Highlink material and initiator 2-15% by weight of the Highlink material gave good results.

When the Highlink OG 108-53 was replaced by Highlink OG 108-31 (30% silica by weight), the toner did not transfer well to the coated material.

Various amine anchorage agents were used in various experiments to determine their suitability. To 45 gr. Highlink OG 103-53 were added 2.5 grams of Irgacure 184 (CIBA) photoinitiator. The mixture was mixed until the powder was totally incorporated. Then in various experiments 2.5 grams of diamine terminated Poly(propylene oxide) (molecular weight 230, amine content 8.45 meq.), monoamine terminated Poly(propylene oxide) (molecular weight 600, amine content 1.66 meq.) or triamine terminated Poly(propylene oxide) (molecular weight 480, amine content 6.45 meq.). The various materials were wire rod coated onto Melinex PET films. The coating was cured immediately by exposure to about 46 joules/cm² of UV light. The coating weight was estimated at about 15 gm/m².

These coated PET sheets were printed on in an OmniumTM CardPressTM printer. All the samples showed good transfer of toner to the sheets. The diamine showed good fixing, the triamine showed good to fair fixing and the monoamine showed only fair fixing.

These results demonstrate the dependence of adhesion fixing characteristics on the amine content of the coating.

The present invention has been described with reference to the best mode for carrying out the invention known to the inventors at the time of filing and using toner and printing systems which are readily available to them. It should be understood that the present invention is believed to be applicable to a wide variety of toners, binders and substrate. As used herein, the terms "include" "have" and "comprise" and their conjugates mean "including but not necessarily limited to".

CLAIMS

1. A printing method comprising:
providing a substrate having a surface coated with a coating comprising at least 25%
5 nano-silica by weight; and
printing on the coated surface with a liquid toner comprising pigmented polymer
particles and a carrier liquid.
2. A printing method according to claim 1 wherein the coating comprises an acrylic
10 material.
3. A printing method according to claim 2 wherein the acrylic material comprises a cross-
linked polyacrylic ester.
- 15 4. A printing method according any of the preceding claims wherein the coating is UV
cured.
5. A printing method according to any of the preceding claims wherein the coating
comprises at least 30% silica.
20
6. A printing method according to claim 5 wherein the coating comprises at least 35%
silica.
7. A printing method according to claim 6 wherein the coating comprises at least 40%
25 silica.
8. A printing method according to claim 7 wherein the coating comprises at least 45%
silica.
- 30 9. A printing method according to claim 8 wherein the coating comprises at least 50%
silica.
10. A printing method according to any of the preceding claims wherein the silica has a
size of between 5 and 50 nanometers.

11. A printing method according to claim 10 wherein the silica has a size of between 10 and 40 nanometers.
- 5 12. A printing method according to claim 11 wherein the silica has a size of between 10 and 20 nanometers.
13. A printing method according to claim 12 wherein the silica has a size of about 16 nanometers.
- 10 14. A printing method according to any of the preceding claims wherein the silica is not chemically bonded to the rest of the coating.
- 15 15. A printing method according to any of claims 1-13 wherein the silica is chemically bonded to the rest of the coating.
16. A printing method according to any of the preceding claims wherein the coating further comprises an anchorage agent.
- 20 17. A printing method according to claim 16 wherein the anchorage agent comprises an amine material.
18. A printing method according to claim 17 wherein the amine material comprises a diamine terminated substance.
- 25 19. A printing method according to claim 17 wherein the amine material comprises a monoamine terminated substance.
20. A printing method according to claim 17 wherein the amine material comprises a triamine terminated substance.
- 30 21. A printing method according to any of claims 18-20 wherein the substance is Poly(propylene oxide).

22. A printing method according to claim 18 wherein the substance is Poly-oxyethylene.
23. A printing method according to any of the preceding claims wherein the substrate and the pigmented particles are both acidic.
- 5 24. A printing method according to any of the preceding claims wherein the substrate is coated with a polyamide coating between the coating containing silica and the substrate.
- 10 25. A printing method according to any of the preceding claims wherein the substrate is PVC.
26. A printing method according to any of claims 1-24 wherein the substrate is PET.
- 15 27. A printing method according to any of claims 1-24 wherein the substrate is polycarbonate.
28. A printing method according to any of the preceding claims wherein the coating forms a substantially smooth surface.
- 20 29. A printing method according to any of the preceding claims wherein the substrate is a sheet of material.
30. A printing method according to any of claims 1-28 wherein the substrate is a disk.
- 25 31. A printing method according to any of the preceding claims wherein the surface of the coating is film.
32. A printing method according to claim 31 wherein the coating is smooth.
- 30 33. A substrate comprising:
a sheet of polymer; and
a printable coating in the form of a film, on the polymer sheet comprising at least 25% nano-silica by weight of total solids.

PDX A02

34. A coated substrate according to claim 33 wherein the coating comprises an acrylic material.
35. A coated substrate according to claim 34 wherein the acrylic material comprises a cross-linked polyacrylic ester.
36. A coated substrate according any of claims 33-35 wherein the coating is UV cured.
37. A coated substrate according to any of claims 33-36 wherein the coating comprises at least 30% silica.
38. A coated substrate according to claim 37 wherein the coating comprises at least 35% silica.
39. A coated substrate according to claim 38 wherein the coating comprises at least 40% silica.
40. A coated substrate according to claim 39 wherein the coating comprises at least 45% silica.
41. A coated substrate according to claim 40 wherein the coating comprises at least 50% silica.
42. A coated substrate according to any of claims 33-41 wherein the silica has a size of between 5 and 50 nanometers.
43. A coated substrate according to claim 42 wherein the silica has a size of between 10 and 40 nanometers.
44. A coated substrate according to claim 43 wherein the silica has a size of between 10 and 20 nanometers.
45. A coated substrate according to claim 44 wherein the silica has a size of about 16 nanometers.

46. A coated substrate according to any of claims 33-45 wherein the silica is not chemically bound to the rest of the coating.
- 5 47. A coated substrate according to any of claims 33-45 wherein the silica is chemically bound to the rest of the coating.
48. A coated substrate according to any of claims 33-46 wherein the coating further comprises an anchorage agent.
- 10 49. A coated substrate according to claim 48 wherein the anchorage agent comprises an amine material.
50. A coated substrate according to claim 49 wherein the amine material comprises a
- 15 diamine terminated substance.
51. A coated substrate according to claim 49 wherein the amine material comprises a monoamine terminated substance.
- 20 52. A coated substrate according to claim 49 wherein the amine material comprises a triamine terminated substance.
53. A coated substrate according to any of claims 50-52 wherein the substance is Poly(propylene oxide).
- 25 54. A printing method according to claim 50 wherein the substance is Poly-oxyethelene.
55. A coated substrate according to any of claims 33-54 wherein the substrate is acidic.
- 30 56. A coated substrate according to any of claims 33-54 wherein the substrate is coated with a polyamide coating between the coating containing silica and the sheet.
57. A coated substrate according to any of claims 33-56 wherein the sheet is PVC.

58. A coated substrate according to any of claims 33-56 wherein the sheet is PET.
59. A coated substrate according to any of claims 33-56 wherein the sheet is polycarbonate.
- 5 60. A coated substrate according to any of claims 33-59 wherein the coating is smooth.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/22172 A1(51) International Patent Classification: G03G 7/00,
9/12, 9/13, B41M 5/00

(21) International Application Number: PCT/IL99/00510

(22) International Filing Date:
22 September 1999 (22.09.1999)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): INDIGO
N.V. (NL/NL); 5 Limburglaan Street, NL-6221SH Maas-
tricht (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ALMOG, Yacov
(IL/IL); 2 Halutz Street, 76251 Rehovot (IL). BRAN-
DRISS, Sergio (IL/IL); 11 Yavetz Street, 76252 Rehovot
(IL).(74) Agents: FENSTER, Paul et al.; Fenster & Company
Patent Attorneys, LTD., P.O. Box 10256, 49002 Petach
Tikva (IL).(81) Designated States (national): AE, AL, AM, AT, AU, AZ,
BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK,
DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL,
IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU,
LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO,
RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG,
US, UZ, VN, YU, ZA, ZW.(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent
(AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU,
MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: SUBSTRATE COATING FOR IMPROVED TONER TRANSFER AND ADHESION

(57) Abstract: A printing method comprising: providing a substrate having a surface coated with a coating comprising at least 25% silica; and printing on the coated surface with an ink comprising pigmented polymer particles and a carrier liquid.

WO 01/22172 A1

Docket No.
UDX

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SUBSTRATE COATING FOR IMPROVED TONER TRANSFER AND ADHESION

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on September 22, 1999 as United States Application No. or PCT International Application Number PCT/IL99/00510 and was amended ~~on~~ as in the annexes to the International Preliminary Examination Report

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

Paul Fenster, Reg. No. 33,877

Maier Fenster, Reg. No. 41,016

Phillip A. Weiss, Reg. No. 19,863

Yaakov Schatz, Reg. No. 44,320

William H. Dippert, Reg. No. 26,723

Michael I. Wolfson, Reg. No. 24,750

R. Lewis Gable, Reg. No. 22,479

Send Correspondence to: William H. Dippert, Esq.
c/o Cowan, Liebowitz and Latman, P.C.
1133 Avenue of the Americas
New York, NY 10036-6799

Direct Telephone Calls to: (name and telephone number)
William H. Dippert (212) 790-9200

1-00

Full name of sole or first inventor	
<u>Yaakov ALMOG</u>	
Sole or first inventor's signature	Date
<u>Y. Almog</u> x	x <u>7/27/02</u>
Residence	
<u>16 Dafna Street, Nes-Ziona 74064, Israel</u> <u>ILX</u>	
Citizenship	
<u>Israel</u>	
Post Office Address	
<u>16 Dafna Street, Nes-Ziona 74064, Israel</u>	

2-00

Full name of second inventor, if any	
<u>Sergio BRANDRISS</u>	
Second inventor's signature	Date
<u>SBR</u> x	x <u>7/27/02</u>
Residence	
<u>11 Yavetz Street, Rehovot 76252, Israel</u> <u>ILX</u>	
Citizenship	
<u>Israel</u>	
Post Office Address	
<u>11 Yavetz Street, Rehovot 76252, Israel</u>	